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Duplexiphane: A Polyaromatic Receptor Containing Two Adjoined Δ-Shaped Cavities for an Efficient Hopping of a Single Silver Cation

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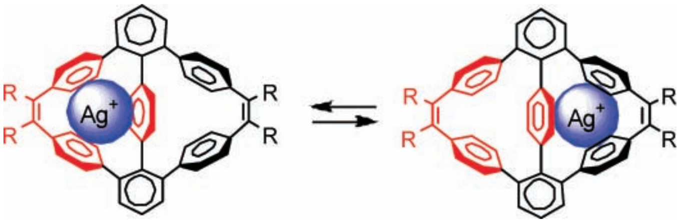
ABSTRACT



A simple synthesis of a polyaromatic receptor (i.e., duplexiphane) containing two adjoined Δ-shaped cavities is accomplished via an intramolecular (double) McMurry coupling, and its structure is established by X-ray crystallography. The binding of silver cation to duplexiphane showed that it binds only a single silver cation with significantly higher efficiency (>100 times) than a model compound containing only one π-prismand-like cavity, and the single silver cation hops intramolecularly between the two adjoined cavities in duplexiphane.

The design and syntheses of macromolecular receptors that bear two or more aromatic groups in cofacially oriented arrays continues to attract attention owing to their potential applications in the areas of electrical conductors and photoresponsive devices.[1−3]

Among the well-known receptors, π-prismand (**1**)[4a] and a structurally analogous deltaphane (**2**)[4b] contain "Δ"-shaped cavities that are especially efficacious for binding a variety of metal cations, such as Ag^+, Tl^+, Ga^+, etc.[4] The X-ray crystallographic analyses of Ag^+ complexes of **1** and **2**, in solid-state, showed that a single silver cation is bound to only one of the faces of the "Δ"-shaped cavities. However, the simplicity of the ^{1}H/^{13}C NMR spectra of the Ag^+ complexes of both **1** and **2**, in solution, indicated that the bound silver cation is highly (kinetically) labile and may undergo back and forth shuttling through the cylindrical cavities, e.g., Figure 1.[4a,b]

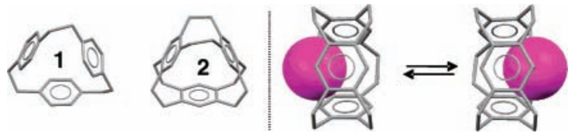


Figure 1. A back and forth shuttling of a single silver cation (pink ball) through the cylindrical cavities of π-prismand (**1**) and deltaphane (**2**).

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(1) (a) Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. *Coord. Chem. Rev.* **2000**, *205*, 59. (b) Ikeda, M.; Tanida, T.; Takeuchi, M.; Shinkai, S. *Org. Lett.* **2000**, *2*, 1803. (c) Lindeman, S. V.; Rathore, R.; Kochi, J. K. *Inorg. Chem.* **2000**, *39*, 5707 and references therein.

(2) (a) Heirtzler, F. R.; Hopf, H.; Jones, P. G.; Bubenitachek, P.; Lehne, V. *J. Org. Chem.* **1993**, *58*, 2781. (b) Gano, J. E.; Subramaniam, G.; Birnbaum, R. *J. Org. Chem.* **1990**, *55*, 4760. (c) Yang, R.-H.; Chan, W.-H.; Lee, A. W. M.; Xia, P.-F.; Zhang, H.-K.; Li, K. *J. Am. Chem. Soc.* **2003**, *125*, 2884. (d) Rathore, R.; Chebny, V. J.; Abdelwahed, S. H. *J. Am. Chem. Soc.* **2004**, *127*, 8012.

(3) (a) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Sugimoto, K. *Inorg. Chem.* **1997**, *36*, 4903. (b) Munakata, M.; Wu, L. P.; Ning, G. L.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Macao, Y. *J. Am. Chem. Soc.* **1999**, *121*, 4968.

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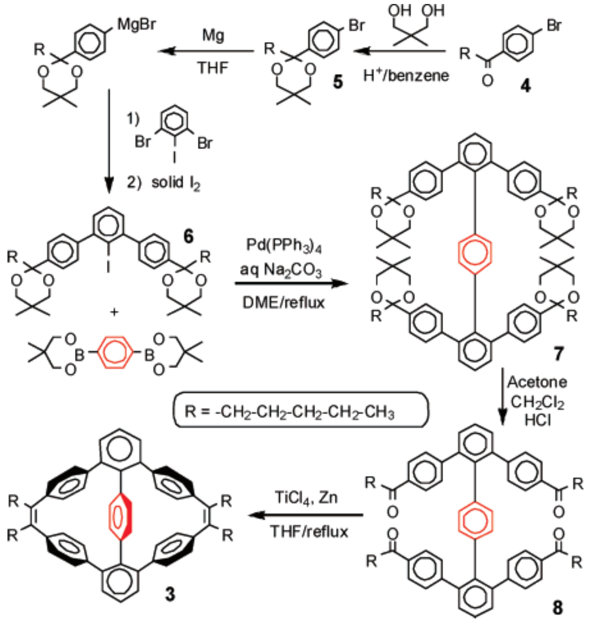
It was conjectured that such receptors, if assembled, in a continuous electronically coupled array, may allow the long-range transport of a metal ion for the potentially interesting applications in the emerging areas of molecular electronics and nanotechnology.[5]

Unfortunately, neither **1** nor **2** is easily accessible nor readily amenable to structural modifications for such applications.[6] Therefore, we envisioned a structure with two adjoined π-prismand-like (or Δ-shaped) cavities that can be easily accessed using standard synthetic procedures (see structure **3** in Scheme 1) and which would hold the potential to be readily tailored for incorporation into polymeric structures or for the deposition onto various surfaces by changing the "R" groups. Furthermore, the two electronically coupled, Δ-shaped cavities in **3**, which is referred to hereafter as *duplexiphane*,[7] will allow us to probe the fluxionality of the silver cation in the [**3**, Ag^+] complex.

Scheme 1. Synthetic Scheme for the Preparation of **3**



Thus, herein we will describe a versatile synthesis and X-ray crystallographic structural characterization of duplexiphane (**3**) and delineate, with the aid of ^1H NMR spectroscopy and a model compound containing only one "Δ"-shaped cavity, that it binds only a single silver cation which most likely hops between the two adjoined cavities.[8]

The synthesis of **3** was accomplished in five steps (Scheme 1) using readily available starting materials in excellent overall yield. Thus, following the procedure of Hart and coworkers,[9] a reaction of freshly prepared Grignard reagent from protected 4-bromohexanophenone **5** (4 equiv) with 2,6-dibromoiodobenzene[9] in tetrahydrofuran at 22 °C for 24 h followed by a quenching of the reaction mixture with iodine at 0 °C afforded 2,6-diaryliodobenzene **6**, in a one-pot procedure, in 66% yield. The diaryliodobenzene **6** was subjected to a Suzuki coupling reaction with 1,4-benzenediborate ester in refluxing dimethoxyethane in the presence of aqueous sodium carbonate and a catalytic amount (2 mol %) of $Pd(PPh_3)_4$ for 24 h.

The crude **7**, from above, was hydrolyzed to the corresponding tetraketone **8** in a 2:1 mixture of dichloromethane/acetone containing 5% (v/v) conc. hydrochloric acid at 22 °C, and the resulting material was purified by column chromatography to afford **8** in 68% overall yield in two steps. The tetraketone **8**, whose structure was confirmed by X-ray crystallography, was then subjected to an intramolecular (double) McMurry coupling under mild dilution to afford the desired duplexiphane (**3**) in excellent yield (72%). The molecular structure of **3** was easily established by ^1H and ^{13}C NMR spectroscopy and further confirmed by high-resolution mass spectrometry (see the Supporting Information).

The unequivocal structural confirmation of **3** was obtained by X-ray crystallography as shown by an ORTEP diagram and by a space-filling representation in Figure 2. A comparison of the geometrical parameters of **3** with **1** and **2** indicated that the size of the internal Δ-shaped cavity is characteristically similar in all three compounds, i.e., an average distance from its center to the centers of the three benzene rings is ∼2.6 Å. Moreover, the two Δ-shaped cavities in **3** are geometrically identical as the molecule occupies a crystallographic center of symmetry. On the basis of the structural similarity of the cavities in **3** with that of **1** and **2**, one would advocate that it should bind Ag^+ with more or less similar efficiency as that of **1** and **2**.

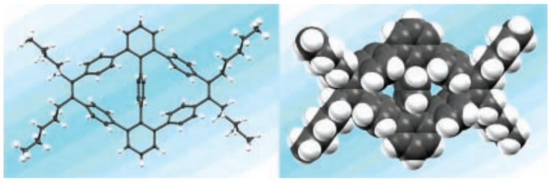


Figure 2. Molecular structure of **3** shown as an ORTEP diagram (left) and as a space-filling representation (right).

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(4) (a) Pierre, J. L.; Baret, P.; Chautemps, P.; Armand, M. *J. Am. Chem. Soc.* **1981**, *103*, 2986. (b) Kang, H. C.; Hanson, A. W.; Eaton, B.; Boelelheide, V. *J. Am. Chem. Soc.* **1985**, *107*, 1979. (c) Pierre, G.; Baret, P.; Chautemps, P.; Pierre, J. L. *Electrochim. Acta* **1983**, *28*, 1269. (c) Schmidbaur, H.; Hager, R.; Huber, B.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 338. (d) Probst, T.; Steigelmann, O.; Riede, J.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1397.

(5) (a) Petty, M. C.; Bryce, M. R. In *Introduction to Molecular Electronics*; Bloor, D., Ed.; Oxford University Press: New York, 1995. (b) Maiya, B. G.; Ramasarma, T. *Curr. Sci.* **2001**, *80*, 1523.

(6) Compare: Heirtzler, F. R.; Hopf, H.; Jones, P. G.; Bubenitschek, P. *Tetrahedron Lett.* **1995**, *36*, 1239.

(7) The term "duplexiphane" was coined based on the suggestion by our colleague James R. Kincaid who pointed out that the structure of **3** conceptually resembles that of a "duplex", a house partitioned to accommodate two residents.

(8) For other examples of metal-ion hopping, see: (a) Ohseto, F.; Sakaki, T.; Araki, K.; Shinkai, S. *Tetrahedron Lett.* **1993**, *34*, 2149. (b) Walker, A. V.; Tighe, T. B.; Cabarcos, O. M.; Reinard, M. D.; Haynie, B. C.; Uppili, S.; Winograd, N.; Allara, D. L. *J. Am. Chem. Soc.* **2004**, *126*, 3954. (c) Berg, D. J.; Sun, J.; Twamley, B. *Chem. Commun.* **2006**, 4019.

(9) Du, C. J. F.; Hart, H.; Ng, K. K. D. *J. Org. Chem.* **1986**, *51*, 3162.

The binding of silver cation to **3** was monitored by the changes in the ^{1}H NMR spectrum of **3** in chloroform-*d* (0.015 M) by an incremental addition of substoichiometric amounts of a solution of silver trifluoromethanesulfonate (0.23 M) in 1:1 mixture of chloroform-*d* and methanol-d_4. The addition of the increments of Ag$^+$ solution showed considerable changes (i.e., broadening and shifts) in the aromatic signals only up to the addition of one equivalent of Ag$^+$ solution, as shown in Figure 3. It is noteworthy that the ^{1}H NMR spectrum remained unchanged upon further addition of Ag$^+$ solution (i.e., beyond 1 equiv).

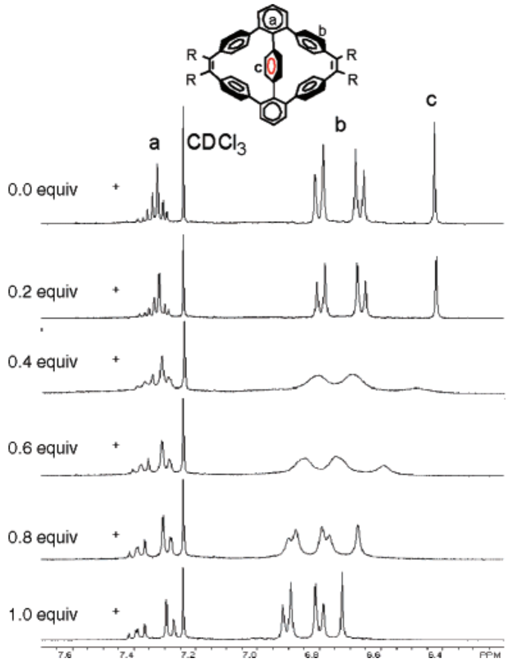
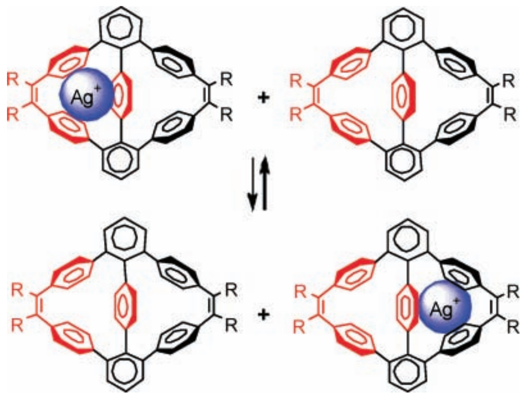


Figure 3. Partial ^{1}H NMR spectra of **3** obtained upon an incremental addition of CF_3SO_3Ag in $CDCl_3$-CD_3OD at 22 °C.

A careful examination of the ^{1}H NMR spectra in Figure 3, revealed that near the 0.5 equiv point (of Ag$^+$ titrations), the NMR signals in Figure 3 are considerably broadened, which however, become sharp when a complete equivalent of Ag$^+$ solution is added. Such a broadening of the ^{1}H NMR signals near the 0.5 equiv point suggests that the *intermolecular* exchange between [**3**, Ag$^+$] and uncomplexed **3** is rather slow at 20 °C, i.e., Scheme 2.[10]

Scheme 2. *Intermolecular* Exchange between [**3**, Ag$^+$] and Uncomplexed **3**



The *intermolecular* exchange process between [**3**, Ag$^+$] and uncomplexed **3** was further confirmed by the observation of the identical broadened NMR signals (Figure 3) when equimolar amounts of [**3**, Ag$^+$] and uncomplexed **3** were mixed. Such an observation of slow *inter*-molecular exchange between [**3**, Ag$^+$] and uncomplexed **3** suggests that a single silver cation is held tightly by **3** and thus prevents a rapid *inter*-molecular exchange with the uncomplexed **3**.

More interestingly, the observation of a symmetrical ^{1}H NMR spectrum of [**3**, Ag$^+$] complex (i.e., the same number of sharp signals as in the uncomplexed **3**) suggests that the single silver cation must be shuttling back and forth among the two adjoined cavities with a speed faster than the NMR time scale, e.g., Scheme 3.[12]

Scheme 3. *Intramolecular* Exchange of Ag$^+$ among the Two Adjoined Cavities of **3**

In order to probe that a single silver cation undergoes *intra*-molecular hopping in **3** (Scheme 3), we have synthesized[13] a model compound (i.e., **9**) containing only one Δ-shaped cavity (R = *n*-pentyl) and confirmed that the shape and size of the cavity in **9** is identical to that of the pair of adjoined cavities in duplexiphane (**3**) by X-ray crystallography.[13]

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[10] For chemical exchanges, the line shape of the NMR resonances depends on the chemical shift difference between the states involved in the exchange process. In a two-site exchange, coalescence occurs when the exchange rate $k_{\mathrm{ex}} = \pi\Delta\nu/\sqrt{2} = 2.22\Delta\nu$, where $\Delta\nu$ is the chemical shift difference in Hz.[11] In this study, $\Delta\nu$ is around 100 Hz on a 300 MHz instrument. Thus, the slow *intermolecular* exchange rate is expected to be in the vicinity of $\sim$200 s^{-1} at 22 °C, since we observed only one broad peak for each proton. It should be contrasted that an *intermolecular* exchange, akin to Scheme 2, with deltaphane (**2**) was noted[4b] to be much faster than NMR time scale at 22 °C, i.e. >200 Hz.

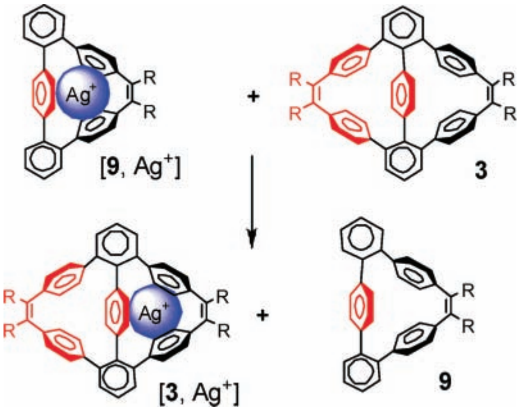
[11] Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy: A Guide for Chemists*; Oxford University Press: New York, 1993, pp 205−234.

[12] The chemical shifts of the two resonances involved in the fast exchange are unknown. We only observed a weight average of the two states. Therefore, we estimated that on a 300 MHz NMR instrument, based on the chemical shifts of Ag$^+$-bound and unbound **3**, the chemical shift difference between these two resonances is roughly 200 Hz. Accordingly, at 22 °C where little chemical exchange was observed, the exchange rate should be at least a couple of orders of magnitude larger than 400 Hz. At −95 °C, the lowest temperature accessible to us, we observed significant line broadening, indicating that the exchange rate at this temperature decreases to $\sim$400 s^{-1}.

[13] The synthetic details and X-ray crystallographic structural characterization of the model receptor **9** will be published separately.

The binding of a single silver cation to model receptor **9** was confirmed by the changes in the ^{1}H NMR spectrum of **9** in chloroform-*d* (0.023 M) by an incremental addition of substoichiometric amounts of a solution of silver trifluoromethanesulfonate (0.37 M) in 1:1 mixture of chloroform-*d* and methanol-d_4. The addition of the increments of Ag^+ solution showed considerable changes in the aromatic signals of **9**, *without any broadening*, only up to the addition of one equivalent of Ag^+ solution. Interestingly, however, when a $CDCl_3-CD_3OD$ solution of [**9**, Ag^+] complex was exposed to an equimolar amount of duplexiphane **3**, it *quantitatively transferred* its bound silver cation to **3** as established by ^{1}H NMR spectroscopy, i.e., Scheme 4 (and Figure S1 in the Supporting Information).

Scheme 4. Quantitative Transfer of Silver Cation from [**9**, Ag^+] to Equimolar **3**



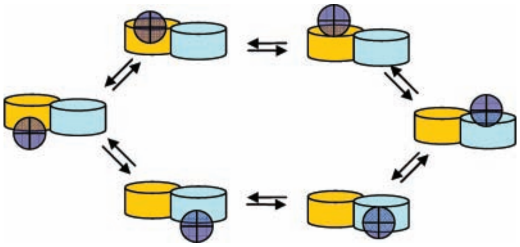
In another experiment, [**3**, Ag^+] complex was exposed up to 4 equiv of model compound **9**, under otherwise identical conditions as in Scheme 4, and its ^{1}H NMR spectrum showed no broadening of the ^{1}H NMR signals of either uncomplexed **9** or the [**3**, Ag^+] complex.

These experiments clearly demonstrate that duplexiphane **3** binds a single silver cation with an efficiency that is *at least 100 times greater* than its model compound **9**, containing a single cavity of similar dimensions as the pair of cavities in duplexiphane **3**. Moreover, the [**3**, Ag^+] complex holds its bound Ag^+ tightly and does not release to the model receptor **9** even when it is present in large excess, indicating that the hopping of a single silver cation in duplexiphane **3** most likely occurs intramolecularly.

In order to estimate the rate of the hopping of the Ag^+ cation in Scheme 3, we attempted variable-temperature NMR spectroscopy. For example, the ^{1}H NMR spectra of [**3**, Ag^+] complex in CD_2Cl_2 containing 5% CD_3OD showed considerable broadening of the signals only at −95 °C, thus suggesting that the coalescence temperature for the hopping process in Scheme 3 was much lower than −95 °C. As such this observation allows us to roughly estimate that the dynamic process in Scheme 3 must occur at a rate faster than ~10,000 Hz.[12]

In summary, we have designed and synthesized a versatile receptor (**3**) with two adjoined Δ-shaped cavities with an expanded (and continuous) π -surface which allows a rapid hopping of a single silver cation among the two electronically coupled cavities with a single aromatic wall, as shown in Scheme 5.

Scheme 5. Possible Mechanism of *intramolecular* Shuttling of a Single Silver Cation between the Two Adjoined, Electronically Coupled Cavities in Duplexiphane **3**



The dramatically enhanced association constant of **3** with Ag^+ in comparison to that of the model receptor **9**, that contains only one cavity, may be reconciled by the fact that there is a considerable entropic gain due to the rapid hopping of Ag^+ on the continuous π-surface of **3**. Furthermore, it can be envisioned that the molecules containing multiple adjoined Δ-shaped cavities would hold potential for the long-range transport of metal cations akin to the natural ion-transport channels found in bilayer membranes.[14] We are actively exploring the preparation of a number of such molecules containing multiple (adjoined) receptor sites for their potential materials' applications.

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Supporting Information Available: Synthetic details, ^{1}H/^{13}C NMR data, and X-ray structural data of **3** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) (a) Gokel, G. W.; Leevy, W. M.; Weber, M. E. *Chem. Rev.* **2004**, *104*, 2723. (b) Weber, M. E.; Gokel, G. W.; Leevy, W. M.; Hughes-Strange, G. B.; Daranciang, D. D.; Ferdani, R.; Gokel, M. R. *Org. Biomol. Chem.* **2005**, *3*, 1647.